

How to Promote Adhesion with Silicones and Silanes



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How to Promote Adhesion with Silicones and Silanes

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Silicones and silanes — used as primers and integral blend additives — help solve a variety of industrial bonding problems

Traditionally, silicones have been known as release agents, valued for their abhesive characteristics. In more recent years, new classes of compounds representing new silicone chemistry have become available which completely reverse this characteristic. When applied as extremely thin coatings, they have the ability to alter strikingly the surface characteristics of many materials, and in a number of instances, this change has led to their use as adhesion promoters in solving difficult and otherwise impossible bonding problems.

Effectiveness in improving the adhesion of a diversity of substances has already been demon-

strated for over two dozen Union Carbide Silicones and Silanes. In most of the current commercial applications, these products are used as primers. However, some of them can and are being employed as integral blend additives, thus eliminating the need for a primer coat. The choice of product for any given application is usually highly specific and depends upon the nature of the materials being bonded, the substrate, and — to some extent — the conditions during bonding and subsequent service.

Dual-functional Chemistry

The silanes which find application as adhesion promoters have

two distinct and different chemical natures. At one end of the molecule are hydrolyzable groups or elements. Typical of these are halogens and alkoxy groups. With water, these react to yield a silanol (SiOH) group which can, in turn, react with other such groups by eliminating water to form Si-O-Si bonds. This is the linkage found in silicones, and gives these polymers their exceptional stability.

Both the monomeric silanes and the polymeric silicones first found use because of the non-reactive nature of the organic groups attached to the silicon. Typical non-reactive groups were methyl, ethyl, and phenyl, and this led to the use of silicones as release coatings, water repellent coatings, and high-temperature resins and elastomers. The newer classes of silicone products have reactive organic groups attached to silicon. These groups are not hydrolyzable but exhibit the typical reactions of the more common organic compounds. Silanes and silicones showing such reactivity are referred to as organo-functional. Among the more common reactive organic groups are vinyl, alkyl amines, methacryloxypropyl, alkyl mercapto, and alkyloxy epoxy radicals.

A system of ambifunctional compounds can be created by combining in the same molecule hydrolyzable groups with one or more organo-functional groups. The dual chemistry of these ambifunctional silanes and silicones makes them

Table I — Flexural Strengths of Glass Cloth Reinforced Laminates

Silane	Flexural Strength, psi		% Retention
	Dry	After 2-hr Boil	
Polyester Resin			
A-172	72,000	68,000	94
A-1100	37,500	18,000	48
None*	60,000	35,000	58
Melamine Resin			
A-172	31,500	28,000	89
A-1100	90,000	85,000	94
None*	38,000	27,000	71
Epoxy Resin			
A-172	75,600	70,000	93
A-1100	81,000	75,000	93
None*	73,600	53,500	75
Phenolic Resin			
A-172	60,000	18,000	30
A-1100	80,000	55,000	70
None*	69,000	14,000	20

*Heat cleaned glass cloth

compatible and reactive with both inorganic and organic materials. It has been established that silanol groups have the ability not only to react with themselves to produce siloxanes or silicones, but also to react with or add to certain inorganic surfaces. These surfaces include those of such materials as metal, glass, ceramic, masonry, and metallic oxides. The molecules orient themselves such that the silicon atom is closest to the surface and is presumably bonded to the surface through a silicon-oxygen covalent bond.

In effect, the exposed surface of the inorganic material is changed chemically to present a surface composed of reactive organic groups. These reactive groups can then enter into chemical combination with a variety of resinous and monomeric systems. The properties of such a composite are considerably different, and generally improved, from those involving the same resin and inorganic material without the silane or silicone at the interface. Molecules with this dual functionality, having the ability to react with both the inorganic surface and the resin, have become known as coupling agents.

Glass Fabric First

The first commercial application of coupling agents was the finishing of glass fabric with functional silanes. The flexural strength of a typical glass fabric — polyester resin laminate is increased from 50,000 psi to 70,000 psi by priming the glass with a vinyl silane. When boiled in water for eight hours, the untreated glass sample will lose 60 per cent or more of its strength while the silane-treated sample loses less than 10 per cent of its strength.

This same concept can be applied to glass roving and a variety of inorganic powders when they are used as fillers in resin systems. A typical case is the use of pulverized silica in an epoxy resin composite. When the silica is first primed with a monolayer of an amino silane which has the ability to react with both the silica and the epoxy resin, the final composite, containing 50 per

cent filler, is about doubled in flexural strength. The wet strength retention of the coupled filler composite is also much greater than that of the untreated specimen.

Such priming has been employed to bond abrasive grits to phenolic resins for grinding wheels, and to bond sand to phenolic resins for shell molds. In the former case, this has considerably extended the range of use of grinding wheels. In the latter case, stronger and less moisture-sensitive molds have been made at lower cost because the

silane permits a more than equivalent economic reduction in the amount of phenolic resin.

Similar treatment can be given to clays, quartz, and such metallic fillers as aluminum and copper in polyester or epoxy resin systems. The result in each case is a system showing improved strength — both dry and wet — and better electrical properties. Important uses include the treatment of sand in filled epoxy concrete patching materials and coatings, and the treatment of metal in filled epoxy materials suitable

Figure 1 — Polysulfide sealant beads on primed and unprimed glass.

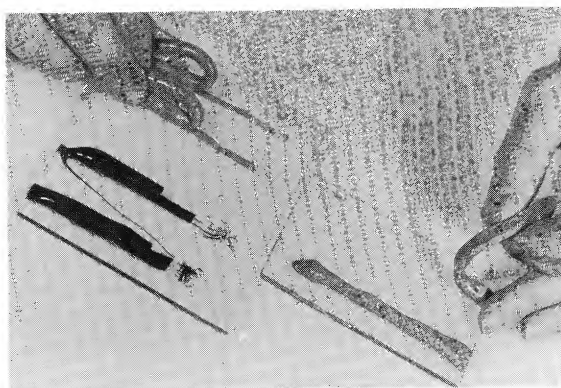


Figure 2 — Polysulfide sealant beads on primed and unprimed steel.

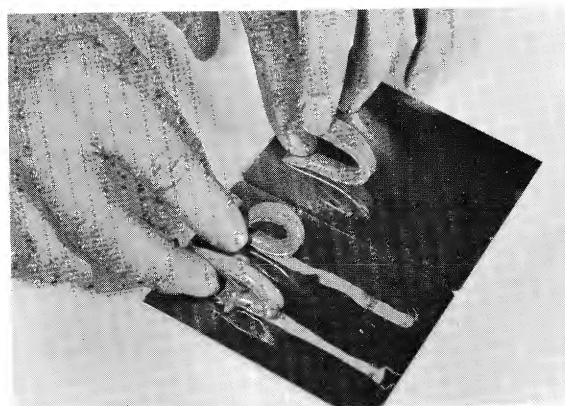
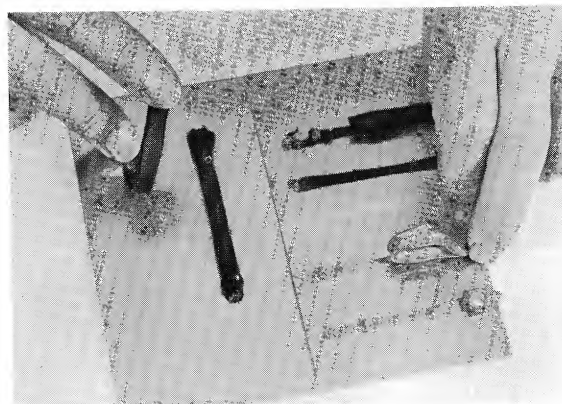


Figure 3 — Polysulfide sealant beads on primed and unprimed aluminum.



In the applications of silane and silicone coupling agents, no single compound serves best for all systems. The performance of silane primers on glass cloth illustrates the specificity of the functional organic groups present in the silane. In the following examples, the specific results of two Union Carbide Silanes [A-172, vinyl tris (2 methoxy ethoxy silane); and A-1100, *gamma* aminopropyltriethoxysilane] with four resin systems serves as evidence of their chemical interaction (Table 1).

The use of coupling agents as integral blend additives is an extension of the theory of performance of these compounds as primers.

As additives, the necessary reactive silane is dissolved directly into the resin system prior to putting it in contact with the inorganic filler, reinforcement, or substrate to be bonded. Under these conditions, and with the selection of the correct silane, there appears to be a migration of the silane from the bulk of the resin to the solid-resin interface.

At the interface, the silane reacts with adsorbed surface moisture to produce silanol groups which, in turn, fasten themselves to the solid. As the resin cures, it reacts with the organo-functional groups to produce the same type of coupling action obtained by pre-treating the solid surface with primer. However, because the process involves migration or diffusion of the silane, it is necessary to permit sufficient time for the surface to become reacted. This time is a function of temperature, resin viscosity, solubility of the silane in the resin, and agitation. The conditions which yield the optimum properties must be determined in each case.

The data presented for glass fiber applications apply generically to the many current uses of silanes and silicones as primers and integral

blend additives for promoting adhesion. The exact nature of the chemical reactions which make them behave as they do is yet to be determined. There may be some actual chemical bonding with the surfaces. Or, the intermolecular force that exists between all molecules may prove even more important.

A review of several important fields of application will illustrate the utility of these unique adhesion promoters.

The use of various elastic cross-linked polymers for sealing joints in modern building construction, the use of such compounds in certain phases of automotive construction, and the possible uses for products of this type in sealing joints in sewer tile and in concrete highways are of immediate interest. Modern construction methods require sealing compounds that do not harden nor oxidize upon exposure, but remain flexible indefinitely. In using such sealants, it is necessary to obtain good adhesion to glass, masonry, and metal.

Inexpensive oil-based caulking and glazing compounds exhibit an

[illegible]

expansion limit of only about 10 per cent and a life of only 5 years when exposed to weather. For the last 25 years, therefore, polysulfide sealants — either one- or two-component products — have come into general use. These materials have a life expectancy of about 20 years and permit joint expansions up to 50 per cent. They have most of the required characteristics, but when the compound/substrate interface is exposed to liquid water or high humidity for extended periods, failure often occurs. The bond to glass is particularly poor.

Pretreatment of the surface with certain silane and silicone primers or premixing the sealant with certain silanes solves the adhesion problem. Previous to the use of silicone primers, some priming — notably the use of phenolic primers on aluminum — was used to help obtain a reasonably good bond with polysulfides. The new silicone and silane products not only surpass all former treatments in improving adhesion, but also make possible for the first time an excellent bond to glass.

Polysulfide Sealants

Three years of commercial experience with polysulfide sealants in place of gaskets on automobile windshields illustrate the value of the new primers on glass. Figures 1, 2 and 3 show beads of polysulfide sealant, one black (carbon filled) and one beige (clay filled) on both primed and unprimed glass, steel and aluminum. The sealant on the untreated surface can be easily stripped clean from the glass, while the primed surface changes the adhesive failure into a cohesive failure. Pulling these samples typically results only in tearing the sealant.

A list of appropriate Union Carbide Silicones and Silanes will be found in Table II for this and the following applications. In the majority of uses, one of the listed products, determined by evaluation tests, will produce optimum adhesion. It has been found that the use of different fillers in the sealant, for example, clays instead of carbon black; or different curing catalyst combinations designed to cure in

Figure 4 — Rigid urethane foam on aluminum.

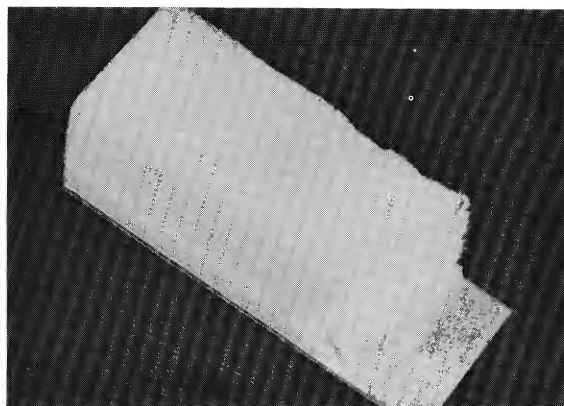


Figure 5 — Silicone rubber bonded to steel.

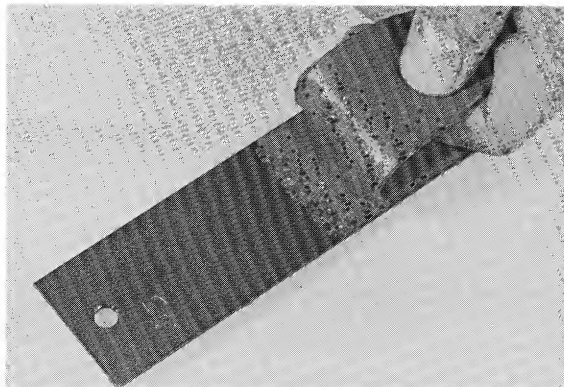


Figure 6 — Clear urethane coating on aluminum.

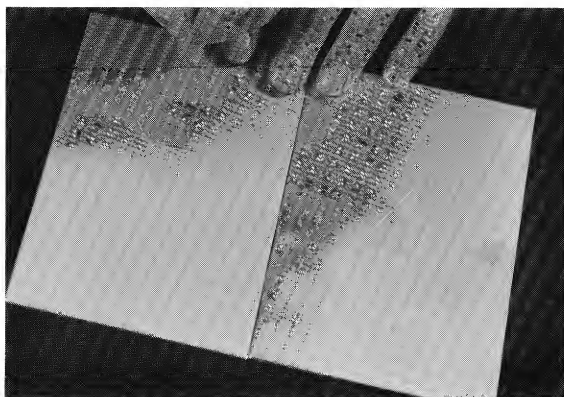
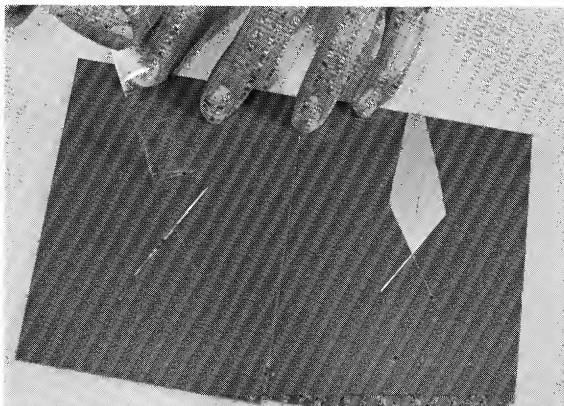


Figure 7 — Pigmented urethane coating on aluminum.

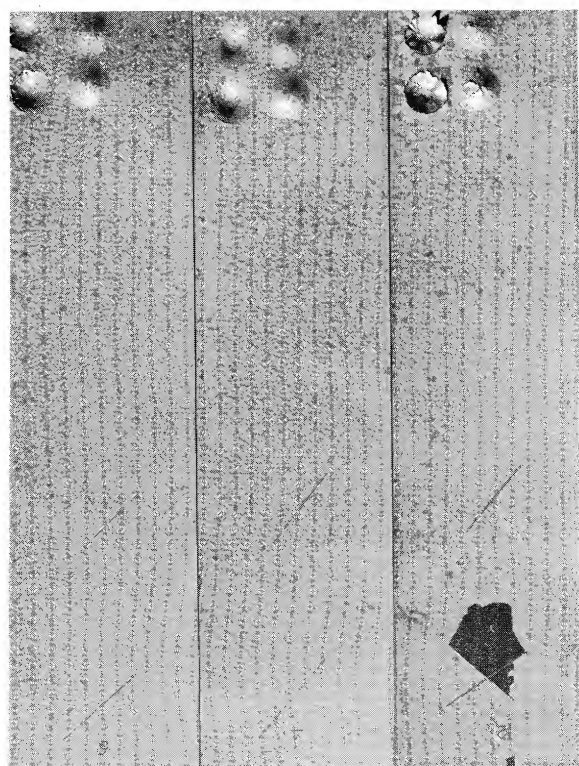


Y-5134 Primer

Y-4486 primer

Control

Gardner Impact Test



← 30 inch #

← 60 inch #

← [Dry Scotch
tape test← [Scotch tape
test after
water immersion
(120 hours)

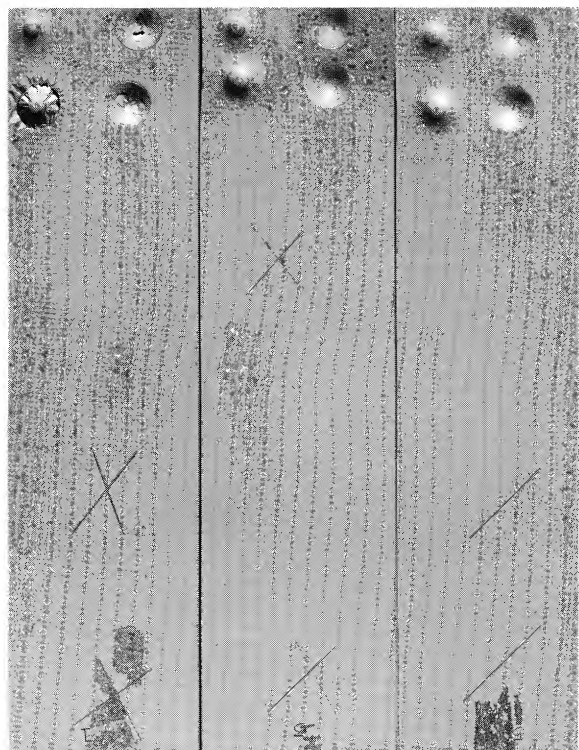
Figure 8 — Aluminum-pigmented acrylic paint applied to aluminum.

Control

Y-4486

Y-5134 primer

Gardner Impact Test



← 30 inch #

← 60 inch #

← [Dry Scotch
tape test← [test after
water immersion
(120 hours)

Figure 9 — Aluminum-pigmented nitrocellulose paint applied to aluminum.

one hour or 8 hours or 24 hours; or different substrates, such as glass, aluminum, or stainless steel, can result in only one particular primer being effective. For this reason, a number of primers are listed for use with polysulfide sealants. Each one has been found to work with a particular commercial polysulfide sealant, but none worked effectively with all the sealants tested.

The recent advent of polyurethane compounds has made available materials which are 50 per cent stronger and tougher than polysulfides and exhibit an elasticity that changes little with age. However, similar problems of bond existed as with the polysulfides. Primers and integral blend additives similar to those used for the polysulfides have been found to perform just as excellently with the polyurethanes.

Rigid Foam

The adhesion of rigid polyurethane foam to aluminum for thermal insulation presents many difficulties. These have been partly solved by surface treatments such as anodizing, combined with primers such as epoxies or acrylics. Even under the best conditions of bonding, however, failures occur under conditions of high humidity. With a silicone-primed aluminum, no failure occurs, even after weeks of water immersion. Moreover, the bond is stronger than the foam itself, as illustrated in Figure 4.

Elastomers

More and more uses for bonded elastomers are found every year. These uses include gaskets, shock absorbers, sealing rings, insulated equipment, and a myriad of other items. As in the case of sealants, silicone, butyl, and urethane elastomers benefit from the use of silicone and silane adhesion promoters. Such substrates as copper, aluminum, and steel are being successfully bonded to silicone rubber, using a silicone primer as illustrated in Figure 5. The metal preparation and primer application techniques are important factors to consider once a suitable silicone is chosen.

The additive approach is illustrated in Table III, where the adhesion of an amine-cured urethane elasto-

mer to glass, steel, and aluminum was measured as normally cured and where an amino silane (A-1100) was added prior to pouring. The 180° pull strengths were measured.

Adhesives

As in all other applications, the silanes and silicones used in an adhesive system must be chosen for their compatibility with the type of material to be employed. Once the selection is made, test samples for each of the primer possibilities can be run to determine which of them produces the strongest bond with a specific adhesive.

Table IV shows typical shear values obtained with two standard epoxy adhesive formulations that were developed for bonding aluminum to itself.

With the preferred silicone primer, improved adhesion results in cohesive failure of the bonding agent itself. However, use of a non-specific silicone primer can, in fact, lead to reduced adhesion.

Coatings

Probably the largest number of varied primer and integral blend additive applications for silanes and silicones is found in the coating field. Included here are both dispersions and solutions of resins that range from thick plastisol coats to much thinner paints, varnishes, and inks.

For example, the addition of 0.5 to 1.0 per cent by weight of A-1100 to epoxy- and acrylic-based inks improves their adhesion to glass to such a degree that the applied ink will continue to adhere after immersion in boiling detergent solutions. The same silane can be blended into vinyl organosols for application to steel or aluminum without a primer. In this use, two parts of A-1100 per 100 parts of resin, after curing, give excellent salt spray and humidity resistance.

The newer urethane coatings are finding increasing applications because of their abrasion resistance and durability. However, when exposed to water attack there can be a complete loss of adhesion to many substrates. Figures 6 and 7 show two commercial urethane coatings, one clear and one pigmented. After

scribing and immersing in water for 24 hours, only the silicone-primed panels showed no loss of adhesion and were not removed by adhesive tape.

Conventional paint coatings also show improved adhesion when applied over silicone primers. Figures 8 and 9 illustrate commercial acrylic- and nitrocellulose-based aluminum paints applied to aluminum. Both primers show improved ad-

hesion measured by impact and reverse impact, and by adhesive tape peeling after 120 hours water immersion.

Only a few of the countless applications in which silicone and silane adhesion promoters are now employed have been covered. Whatever the adhesive system, chances are that one of these adhesion promoters can improve the bond strength economically.

Table III — Adhesive Strength of Urethane Elastomer to Glass — Steel — Aluminum

(lb. pull/inch width)

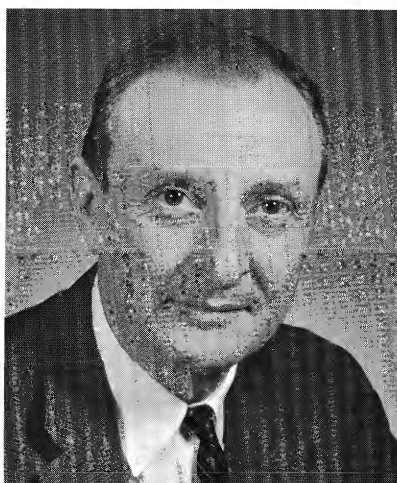
Initial	Glass	Steel	Aluminum
Control	1.2	8.1	3.5
Silane Added	40.0	23.0	14.1
After 2 Months			
Control	< 0.1	3.9	0.5
Silane Added	37.9	20.5	14.4

Table IV — Typical Shear Values* for Two Epoxy Adhesive Formulations for Bonding Aluminum-to-Aluminum

Primer on Test	Failure Type	Adhesive A		Adhesive B	
		psi	Failure Type	psi	Failure Type
Control	Adhesive	1,620	Adhesive	1,500	
Y-4310	"	1,220	"	700	
Y-2500	Cohesive	2,050	Cohesive	2,250	
Y-4526	"	2,050	"	2,160	

*ASTM D-1002.

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